# HIGH STRENGTH TITANIUM COPPER ALLOY, MANUFACTURING METHOD THEREFOR, AND

#### TERMINAL CONNECTOR USING THE SAME

#### **BACKGROUND OF THE INVENTION**

Field of the Invention

[0001] The present invention relates to high strength titanium copper alloys, which are superior in bending properties, used for terminal connectors and other electronic components, a manufacturing method therefor, and a terminal connector using the same. The invention also relates to high strength titanium copper alloys, which are optimal for a fork-shaped contact demanding high strength for raw material of metal material, a manufacturing method therefor, and a fork-shaped connector using the titanium copper alloy.

## Description of the Related Art

[0002] Copper alloy containing titanium such as C1990 (hereinafter called titanium copper alloy) is noted for its superior workability and mechanical strength, and is widely used in terminal connectors and in other applications for electronic components. On the other hand, the trend toward miniaturization of electronic components is recently stronger than before, and the wrought product of copper alloys for electronic components are required to be even thinner in thickness to cope with this trend. In a view of the thinness of material, higher strength of the material itself is required to maintain the contact pressure of the connector, and a small bending radius is required in the bending process of components to fulfil

the function in a limited space. That is, the titanium copper alloy is required to have contrary characteristics of high electrical conductivity and high strength and superior bending properties.

[0003] Furthermore, along with the advancement in high density mountings for cellular phones, digital cameras, video cameras, etc., metal members for electronic components such as terminal connectors and lead frames are bent and formed in very complicated shapes, and an superior bending properties is required, in particular, in addition to having high strength.

[0004] Under such circumstances, in order to improve bending properties and the stress relief rate of the titanium copper alloy, much has been reported about the manufacturing method of solution treatment of crystals, under heat treatment condition, not exceeding a grain size of  $20 \,\mu m$  (for example, Japanese Patent Application Laid-Open No. 7-258803). However, to satisfy the requirement of bending properties of the copper alloy material used in recent electronic components such as terminal connectors, at present, such an improved titanium copper alloy does not have sufficient bending properties. To satisfy the requirements for titanium copper alloy, it is important to improve the correlation of strength and bending properties, and for this purpose, it is also necessary to improve the manufacturing method for titanium copper alloy.

[0005] Hitherto, where the required tensile strength of copper alloy for electronic component was at a medium level of about 500 to 800 MPa, brass, phosphor bronze, or nickel silver is used, or where a higher electrical conductivity is required, Cu-Ni-Si, Cu-Cr-Zr, or Cu-Cr-Sn copper alloy is used, and where a high strength over about 900 MPa is required, beryllium copper or titanium copper is used.

[0006] Recently, demand for FPCs (flexible printed circuit boards) is increasing, and the connectors for FPCs are modified. The fork-shaped connector is used in a connector for an FPC, and in contrast to the general-purpose connector used on the surface contacting with metal material, it is designed to contact with the circuit board on the fracture of the copper alloy plate. Accordingly, a bending process is not necessary, and the fork-shaped connector is required to have a high strength, in the first place, if the bending properties are not favorable.

[0007] Specifically, the fork-shaped connector is required to have a tensile strength of at least 1000 MPa or more, and in order to be applicable to versatile designs, a tensile strength of 1200 MPa or more is necessary.

[0008] Stainless steel of high strength, for example, SUS301 has a tensile strength exceeding 1200 MPa, but stainless steel is low in electrical conductivity, about 2.4% IACS, and cannot be used for a fork-shaped connector. A fork-shaped connector is required to have an electrical conductivity of at least 10% IACS.

[0009] As a copper alloy having a tensile strength of 1200 MPa or more, beryllium copper is well known. As a high strength copper alloy, titanium copper is also usable, but in order to have a tensile strength of 1200 MPa or more, titanium must be contained at 4% by mass, and it further requires special treatment such as MTH (aging, working, heating) (Lecture on Modern Metal Materials 5, Nonferrous Materials, p. 78 (Japan Society of Metallurgy), etc.).

[0010] However, titanium copper containing Ti at 4% by mass is poor in workability, and is likely to crack in hot rolling or to develop edge cracks in cold rolling, and it is difficult to manufacture at high proof stress industrially, and it is also difficult to sell commercially as material for

electronic components. The MTH treatment is a process of cold rolling of titanium copper after aging, followed by heat treatment, but cold rolling of titanium copper alloy after aging is likely to cause edge cracking, and it is difficult to manufacture.

[0011] On the other hand, in the conventional manufacturing method for titanium copper containing 3% by mass of Ti (C1990), the obtained tensile strength is about 1000 MPa at most. Japanese Patent Application Laid-Open No. 7-258803 discloses a manufacturing method of solution treatment of titanium copper alloy in the heat treating condition in which the crystal grain does not exceed 20  $\mu$ m, and it is known that a material which is superior in bending properties and is not lowered in strength can be manufactured as compared with similar conventional materials; however, titanium copper of high strength is not obtainable. Therefore, as a copper alloy having a tensile strength of 1200 MPa, there was no copper alloy other than beryllium copper, which monopolized the market. [0012] However, beryllium copper is not an ideal copper alloy; it is inferior to titanium copper in stress relief characteristics, and is not fully satisfactory. Therefore, in a titanium copper alloy containing Ti at 2.0 to 3.5% by mass, if the tensile strength could be improved to 1200 MPa or more, the alloy would be an optimal high strength copper alloy having the stress relief characteristics, and hence improvement is anticipated.

#### SUMMARY OF THE INVENTION

[0013] The invention is made in light of above circumstances, and it is hence an object thereof to provide a titanium copper alloy as a terminal connector material which is enhanced in strength without having lowered bending properties. It is also an object of the invention to provide a high

strength titanium copper alloy having a tensile strength of 1200 MPa or more, equivalent to that of beryllium copper, and an electrical conductivity of 10% IACS or more, a manufacturing method thereof, and an electronic component using the same high strength titanium copper alloy, in particular, a fork-shaped connector.

[0014] The inventors attempted to adjust conditions of the final recrystallization annealing of titanium copper alloy (conditions of solution treatment), and the subsequent cold rolling and aging conditions, researched the relationship between characteristic values after final heat treatment, and discovered that a titanium copper alloy material enhanced in strength without having lowered bending properties can be obtained stably. [0015] The present invention is made on the basis of the above knowledge. A first aspect of the present invention provides a high strength titanium copper alloy consisting of Ti at 2.0% by mass or more to 3.5% by mass or less; the balance of copper and inevitable impurities; and an average grain size of 20  $\mu$ m or less; the alloy further comprising a 0.2% proof stress expressed by "b" of 800 N/mm² or more; and a bending radius ratio (bending radius/sheet thickness) not causing cracking as expressed by "a" by a W-bending test in a transverse direction to a rolling direction; wherein "a" and "b" satisfy a  $\leq$  0.05xb - 40.

[0016] The second aspect of the invention provides a high strength titanium copper alloy consisting of Ti at 2.0% by mass or more to 3.5% by mass or less; at least one of Zn, Cr, Zr, Fe, Ni, Sn, In, Mn, P, and Si at 0.01% by mass or more to 3.0% by mass or less in total; and the balance of copper and inevitable impurities; the alloy further comprising an average grain size of 20  $\mu$ m or less; a 0.2% proof stress expressed by "b" of 800 N/mm² or more; and a bending radius ratio (bending radius/sheet thickness)

not causing cracking as expressed by "a" by a W-bending test in a transverse direction to a rolling direction; wherein "a" and "b" satisfy  $a \le 0.05xb - 40$ .

[0017] The reasons for setting the numerical values specified above are explained below together with the operation of the invention. In the following explanation, "%" means "% by mass."

A. Ti: 2.0 to 3.5%

[0018] Ti is characterized by inducing spinodal decomposition by aging of Cu-Ti alloy, thereby generating a concentration modulation structure in the matrix, and assuring a very high strength. However, desired reinforcement is not expected if the content is less than 2.0%. If Ti is contained at more than 3.5%, precipitation of grain boundary reaction type is likely to occur, and the strength may be lowered, in contrast, and the workability deteriorates. Hence, the content of Ti is defined in a range of 2.0 to 3.5%.

B. Zn, Cr, Zr, Fe, Ni, Sn, In, Mn, P, Si: 0.01 to 3.0% in total [0019] Cr, Zr, Fe, Ni, Sn, In, Mn, P, and Si are all known to suppress precipitation of grain boundary reaction type without substantially lowering the electrical conductivity of a Cu-Ti alloy, make grain size fine, and increase the strength by aging precipitation. Moreover, Sn, In, Mn, P, and Si are known to increase the strength of a Cu-Ti alloy by solid solution reinforcement. Therefore, one or more elements thereof are added as required. However, if the total content thereof is less than 0.01%, desired effects are not expected. If the total content exceeds 3.0%, the electrical conductivity and workability of the Cu-Ti alloy deteriorate significantly. Therefore, the content of one element or more elements of Zn, Cr, Zr, Fe, Ni, Sn, In, Mn, P, and Si is specified to be in a range of 0.01 to 3.0% in

total.

[0020] Of these additive elements, Zn is expected to suppress heat peel off of solder without lowering the electrical conductivity of a Cu-Ti alloy, and is added most preferably. However, if the content of Zn is less than 0.05%, desired effects are not expected. If the content of Zn exceeds 2.0%, the electrical conductivity and stress relief characteristics deteriorate.

Therefore, the content of Zn is preferred to be in a range of 0.05 to 2.0%.

C. Characteristics of titanium copper alloy

[0021] In order that a titanium copper alloy be used as a terminal connector material, in particular, the bending properties are important because it is used being formed into a complicated part, together with its material strength. In the designing of a part, considerations are given to the 0.2% proof stress as the index of material strength, and the bending properties evaluated by the state of the bending part when it is bent at various bending radii with respect to the material plate thickness. inventors quantitatively analyzed the bending properties depending on the strength and plate thickness required in the recent electronic components, and discovered a specific scale balancing both as explained below. [0022] That is, when the 0.2% proof stress expressed by "b" is 800 N/mm<sup>2</sup> or more, the bending radius ratio (bending radius/sheet thickness) not causing cracking as expressed by "a" by a W-bending test in a transverse direction to a rolling direction, "a" and "b" satisfy  $a \le 0.05xb$  – 40, the high strength and bending properties can be balanced, and the titanium copper alloy can meet recent demands. The 0.2% proof stress of titanium copper alloy is defined to be 800 N/mm<sup>2</sup> or more because the high strength characteristics as a titanium copper alloy cannot be exhibited sufficiently if less than 800 N/mm<sup>2</sup>. In the invention, the grain size is

measured by using the value obtained by the cutting method according to JIS H 0501.

[0023] To enhance the strength of titanium copper alloy, it has been known to reinforce the solid solution by adding alloy elements, reinforce precipitation by adequately controlling the aging temperature, or reinforce by work hardening by adequately controlling the working ratio before aging, and hitherto the desired material characteristics were assured by combining these methods. However, when the strength is enhanced by such reinforcing mechanisms only, the bending properties may deteriorate, and it may fail to reach a desired region of material characteristics. Accordingly, the inventors conducted various tests, and found that there is a relationship between the strength and bending properties with respect to the grain size, and that the average grain size of 20  $\mu$ m is required in order to obtain the above relationship of 0.2% proof stress and bending radius ratio. [0024] Furthermore, in order to enhance the bending properties without lowering the material strength, it is necessary to define the grain size strictly, and to control adequately the final recrystallization annealing condition, cold working ratio, and aging temperature. The invention also provides a terminal connector using such titanium copper alloy. [0025] The manufacturing method for titanium copper alloy of the invention is characterized by performing final recrystallization annealing at a temperature below the borderline L of the  $\alpha$ -phase and the  $\alpha$ +Cu<sub>3</sub>Ti phase shown in Fig. 1.

[0026] It is essential in the invention to specify the final recrystallization annealing condition, and the subsequent cold working and aging conditions. The final recrystallization annealing condition is intended to facilitate the subsequent process, and to adjust the material characteristics and grain size.

to 20  $\mu$ m.

[0027] Hitherto, to manufacture a titanium copper alloy of which the grain size does not exceed 20  $\mu$ m, the grain size was adjusted by adequately controlling the treatment time by determining the treating temperature in a solid solution region of Ti. However, in the case of recrystallization by solution treatment at high temperature and in a short time, since the uniformity of grain size is insufficient, although the strength may be enhanced, the workability is impaired, the characteristics vary widely, and hence it was difficult to stabilize the high strength of titanium copper alloy at a grain size of 20  $\mu$ m or less.

[0028] Accordingly, the inventors made various tests about recrystallization annealing, and discovered that a titanium copper alloy superior in bending properties without lowering the strength and having small variations of characteristics can be obtained, in each composition, by performing recrystallization annealing at a temperature below the borderline L of  $\alpha$ -( $\alpha$ +Cu<sub>3</sub>Ti) which is the borderline of the solid solution-precipitation, that is, in a temperature region partially causing precipitation, instead of temperature region of solid solution of all contained Ti in Cu, for a time so that the average grain size does not exceed 20  $\mu$ m. The temperature y (°C) of  $\alpha$ -( $\alpha$ +Cu<sub>3</sub>Ti) borderline L can be approximated in formula y = 50x + 650, where x (%) is the concentration of Ti. [0029] Meanwhile, as the grain size becomes finer, the bending properties are better, but if the average grain size is less than 3  $\mu$ m, non-recrystallized portion may remain, and the bending properties may deteriorate, and therefore the average grain size should be 20  $\mu$ m or less, more preferably 3

[0030] The cooling rate after recrystallization annealing should be 100°C/sec or more. If the cooling rate is less than 100°C/sec, spinodal

decomposition occurs at the time of cooling, and the material is hardened, and the subsequent working becomes difficult. It is hence preferred to cool the material surface coming out of the heating furnace by water or steam and water, so that the material can be cooled uniformly while maintaining the specified cooling rate.

[0031] Furthermore, in order to obtain such characteristics correlation of 0.2% proof stress and bending properties, aside from the recrystallization annealing condition, it is required to specify the subsequent cold working ratio and aging condition strictly. After recrystallization annealing, almost all Ti of the material is in solid solution, and then it is worked by cold rolling and aged. The working ratio of cold rolling is preferred to be 5 to 70% or less. If it is less than 5%, increase in strength by work hardening is small, and desired strength is not obtained, but when the working ratio exceeds 70%, although a high strength is obtained by adequately controlling the aging condition, the bending properties deteriorate, and the correlation of 0.2% proof stress and bending properties are not obtained. [0032] The aging condition is preferred to be 300°C or more to 600°C or less. If the aging temperature is less than 300°C, aging is not sufficient, and the material strength is not improved. If it is aged at a temperature over 600°C, the solid solution amount of Ti is excessive (the precipitation amount is less), and desired strength is not obtained. The period of aging is preferred to be 1 hour or more to 15 hours or less. If it is less than 1 hour, improvement of strength and electrical conductivity by aging is not expected, or if it exceeds 15 hours, the strength declines due to over-aging. [0033] Accordingly, the titanium copper alloy of the invention is an aging-cured type copper alloy of superior bending properties and high strength, and it is used in the terminal connector of small size in which

superior bending properties and high strength are required. If the contact of the terminal connector is plated before or after press working, the strength and bending properties hardly deteriorate, and the effect of the invention is exhibited.

[0034] Such high strength titanium is generally press worked after the aging process. The inventors discovered that the bending properties are further enhanced by limiting the range of grain size in further narrower bounds while aging after pressing process. That is, the invention according to a third aspect provides a titanium copper alloy which is subjected to an aging process after press working, the alloy consisting of: Ti at 2.0% by mass or more to 3.5% by mass or less; and the balance of copper and inevitable impurities; the alloy further comprising a grain size of 5 to 15  $\mu$ m; wherein cracking does not occur by a W-bending test in a transverse direction to a rolling direction with a bending radius of zero before the aging process, and the hardness of the worked matrix after the aging process is 300 Hv or more, and it is more preferable that it be 310 Hv or more.

[0035] Moreover, the invention according to a fourth aspect provides a titanium copper alloy which is subjected to an aging process after press working, the alloy consisting of: Ti at 2.0% by mass or more to 3.5% by mass or less; at least one of Zn, Cr, Zr, Fe, Ni, Sn, In, Mn, P, and Si at 0.01% by mass or more to 3.0% by mass or less in total; and the balance of copper and inevitable impurities; the alloy further comprising a grain size of 5 to 15  $\mu$ m; wherein cracking does not occur by a W-bending test in a transverse direction to a rolling direction with a bending radius of zero before the aging process, and the hardness of the worked matrix after the aging process is 300 Hv or more, and it is more preferable that it be 310 Hv

or more.

[0036] Such high strength titanium copper alloy is manufactured by performing final recrystallization annealing at a temperature below the borderline of  $\alpha$ -phase and  $\alpha$ +Cu<sub>3</sub>Ti phase to adjust the grain size to 5 to 15  $\mu$ m, and executing final cold rolling at a working ratio of 5 to 50%. The aging conditions may be the same as in the first and second aspects of the invention, and such a manufacturing method is also one of the features of the invention. Furthermore, the third and fourth aspects are also applied in the terminal connector of small size where superior bending properties and high strength are required, and such a terminal connector is also one of the features of the invention.

[0037] The inventors further researched the manufacturing process of titanium copper alloy, and adjusted the hot rolling condition, and the subsequent cold rolling condition and aging condition, and discovered that a high strength titanium copper alloy having a tensile strength of 1200 MPa or more can be obtained stably.

[0038] That is, a fifth aspect of the invention provides a high strength titanium copper alloy consisting of: Ti at 2.0% by mass or more to 3.5% by mass or less; and the balance of copper and inevitable impurities; the alloy further comprising a tensile strength of 1200 MPa or more and an electrical conductivity of 10% IACS or more.

[0039] The sixth aspect of the invention provides a high strength titanium copper alloy consisting of: Ti at 2.0% by mass or more to 3.5% by mass or less; Zn at 0.05% by mass or more to 2.0% by mass or less; at least one of Cr, Zr, Fe, Ni, Sn, In, Mn, P, and Si at 0.01% by mass or more to 3.0% by mass or less in total; and the balance of copper and inevitable impurities; the alloy further comprising a tensile strength of 1200 MPa or more and an

electrical conductivity of 10% IACS or more.

[0040] The high strength titanium copper alloy can be manufactured by hot rolling at a temperature of 600°C or more, cold rolling successively at a working ratio of 95% or more, and aging at temperature of 340°C or more to less than 480°C for 1 hour or more to less than 15 hours while maintaining the state of the matrix after cold rolling.

[0041] The invention further provides a fork-shaped connector using the high strength titanium copper alloy of the fifth or sixth aspect.

[0042] In the fifth and sixth aspects, the reasons for limiting the contents are the same as in the first and second aspects. The reasons for limiting the characteristic values in the fifth and sixth aspects are as follows.

#### (1) Tensile strength

[0043] The fork-shaped connector for FPC differs from the general-purpose connector contacting with the surface of metal material, is designed to contact with the circuit board at the fracture of copper alloy plate, and is not processed by bending. Accordingly, the requirement of prime importance is the strength. In the invention, the strength is evaluated by tensile strength. The required tensile strength of a fork-shaped connector is not sufficient at the tensile strength obtained by general-purpose copper alloy such as brass, phosphor bronze, or nickel silver, but is 1200 MPa or more so as to be applicable to versatile designs as fork-shaped connectors.

# (2) Electrical conductivity

[0044] As the metal material for fork-shaped connector for FPC, the strength is most important, but since the fork-shaped connector is designed to contact at the fracture of metal material, the contact resistance is larger than in other connectors. As a countermeasure, the contact area is plated

with gold, but certain electrical conductivity is also required as metal material. Some stainless steel materials are high in strength, but the electrical conductivity is low, and the heat generated in the contact portion is poorly dissipated. At least, an electrical conductivity of 10% IACS is needed.

[0045] The high strength titanium copper alloy of the fifth and sixth aspects is manufactured in the following method.

[0046] Hitherto, in the manufacturing method for enhancing the strength of titanium copper alloy, after hot rolling, cold rolling and heat treatment, the material is heated (solution treatment) to adjust the grain size at 20  $\mu$ m or less, and the working ratio of final cold rolling and aging temperature are properly controlled, so that a material of tensile strength of about 1000 MPa and superior bending property is manufactured (Japanese Patent Application Laid-Open No. 7-258803). However, considering the manufacturing efficiency, in the Ti amount range of 2.0 to 3.5% by mass, the tensile strength of 1200 MPa or more is not yet achieved in the high strength titanium copper alloy manufactured in this method. As for the MTH treatment mentioned above, the tensile strength of 1200 MPa or more is not yet obtained in the Ti amount range of 2.0 to 3.5% by mass. [0047] In the manufacturing method of the invention, it is essential to specify the "material temperature in hot rolling," "working ratio in cold rolling before aging process," and "aging condition."

# (1) Hot rolling

[0048] Hot rolling is intended to homogenize the cast matrix, and to induce dynamic recrystallization by rolling at higher temperature, so that subsequent processes can be easily performed. If the material temperature is lower than 600°C during hot rolling, titanium copper alloy causes

spinodal decomposition to harden abruptly, and the subsequent cold working is difficult, and the characteristics vary widely. Therefore, the material temperature is kept above 600°C during the hot rolling process. As for cooling after hot rolling, the material hardness unless cooled quickly and the subsequent rolling is difficult, and therefore, by water cooling or the like, the cooling rate of the material is preferred to be 200°C/sec or more.

#### (2) Cold rolling

[0049] So far, the titanium copper alloy was cold rolled and annealed after the hot rolling process, and then cold rolled to a specified sheet thickness, and was further heated (solution treatment) for a short time at a high temperature before aging process. That is, heat treatment is intended to adjust the material characteristics and to make the subsequent processing easier, but since the heat treatment is applied between the hot rolling and the aging, a proper working ratio of cold rolling cannot be set, the strength is lowered, and it is hard to obtain a desired high strength.

[0050] However, by strictly specifying the working condition of hot rolling, a strong working of 95% or more is possible in the subsequent cold rolling. Herein, the working ratio of cold rolling is 95% or more because the working ratio must be specified strictly in order to obtain a tensile strength of 1200 MPa or more by the subsequent aging process, although the strength is generally elevated as the working ratio is higher, and a tensile strength of 1200 MPa or more can be obtained by defining the working ratio at 95% or more.

## (3) Aging

[0051] After the cold rolling process, the material is aged in order to reinforce the strength and improve the elongation, elastic property and

electrical conductivity. The aging temperature is defined in a range of 340°C to less than 480°C, that is, if the aging temperature is less than 340°C, the aging effect is not sufficient, and the strength and electrical conductivity are not improved, but at 480°C or more, since the cold rolling working ratio before aging process is strong working of 95% or more, it may result in over-aging if aged for a short time, and the strength is lowered and desired characteristics are not obtained, and therefore the temperature range of 340°C or more to less than 480°C is specified. [0052] The aging period is 1 hour or more to less than 15 hours, that is, if less than 1 hour, improvement of strength and electrical conductivity by aging is not expected, and if 15 hours or more, the strength is lowered due to excessive over-aging, and hence the aging period is defined in a range of 1 hour or more to less than 15 hours.

[0053] Such high strength titanium copper is generally press worked after the aging process. The inventors discovered that dimensional changes after aging are substantially small. Therefore, the invention according to a seventh aspect provides to a titanium copper alloy which is subjected to an aging process after press working, the alloy consisting of: Ti at 2.0% by mass or more to 3.5% by mass or less; and the balance of copper and inevitable impurities; the alloy further comprising a worked matrix having a hardness of 345 Hv or more after the aging process.

[0054] Furthermore, an eighth aspect of the invention provides a titanium copper alloy which is subjected to an aging process after press working, the alloy consisting of: Ti at 2.0% by mass or more to 3.5% by mass or less; Zn at 0.05% by mass or more to 2.0% by mass or less; at least one of Cr, Zr, Fe, Ni, Sn, In, Mn, P, and Si at 0.01% by mass or more to 3.0% by mass or less in total; and the balance of copper and inevitable impurities;

the alloy further comprising a worked matrix having a hardness of 345 Hv or more after the aging process.

[0055] The high strength titanium copper alloys of the seventh and eighth aspects are manufactured by hot rolling at a temperature of 600°C or more, and cold rolling successively at a working ratio of 95% or more, and such a manufacturing method is also one of the features of the invention. The high strength titanium copper alloys of the seventh and eighth aspects are particularly suited to a fork-shaped connector, and such a fork-shaped connector is also one of the features of the invention.

#### **BRIEF DESCRIPTION OF DRAWING**

[0056] Fig. 1 is a Ti-Cu equilibrium diagram.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

Examples

(Example 1)

[0057] The invention is specifically explained below by referring to example 1 which shows a particularly preferred alloy composition range. First, using electrolytic cathode copper or oxygen-free copper as a raw material, copper alloy ingots (50 mm thick x 100 mm wide x 200 mm long) of various compositions shown in Table 1 (examples) and Table 2 (comparative examples) were melted in a high frequency melting furnace. Consequently, each ingot was heated for 1 hour at a temperature of 850 to 950°C, and was hot rolled, and a plate with 8 mm thick was obtained. At this time, the material temperature after hot rolling was 650°C or more, and the material was cooled in water after hot rolling. The oxide layer on the surface of the sheet was polished and removed, and rolling and

recrystallization annealing were repeated, and after proper pickling, recrystallization annealing (solution treatment) was conducted in the condition of Tables 1 and 2, being followed by cold rolling and aging, and a material having a thickness of 0.2 mm was obtained. After recrystallization annealing, the material was cooled by immersing in water after heat treatment. At this time, the cooling rate was  $200^{\circ}$ C/sec or more, which was confirmed by attaching a thermocouple to the material surface. The table also records the value of temperature of  $\alpha$ -( $\alpha$ +Cu<sub>3</sub>Ti) borderline as approximated in formula (y = 50x + 650). As shown in Table 1, in the invention, recrystallization annealing was conducted at a temperature below the  $\alpha$ -( $\alpha$ +Cu<sub>3</sub>Ti) borderline and within 50°C. [0058]

Table 1

$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Compc	siti	Composition (unit: % by mass)			Manufacturing conditions	g conditions		
$a \cdot (a + Cu_3 \Pi)$ Temperature $(C)$ Average crystal particle size $(D_a)$ processing ratio $(P_a)$ $810$ $T70$ $(C)$ $(I \cdot m)$ $50$ $810$ $770$ $10$ $50$ $780$ $750$ $5$ $40$ $780$ $770$ $10$ $50$ $825$ $770$ $10$ $50$ $825$ $770$ $10$ $50$ $825$ $770$ $10$ $50$ $825$ $770$ $10$ $50$ $800$ $770$ $10$ $60$ $810$ $770$ $10$ $60$ $810$ $770$ $10$ $60$ $810$ $770$ $10$ $60$ $810$ $770$ $10$ $60$ $800$ $770$ $10$ $60$ $90$ $785$ $750$ $10$ $60$ $90$ $780$ $90$ $90$ $90$ $90$ <td< th=""><th></th><th></th><th></th><th>Temperature at</th><th>Recrystalli</th><th>zation annealing condition</th><th>Cold rolling</th><th>Aging condition</th><th>tion</th></td<>				Temperature at	Recrystalli	zation annealing condition	Cold rolling	Aging condition	tion
810         770         10         50           795         750         5         40           780         750         5         40           770         770         5         40           825         770         10         50           800         770         10         50           800         770         10         50           705         750         10         65           800         770         10         65           810         770         10         60           810         770         10         50           800         750         10         50           800         750         10         60           70         785         750         5           800         750         5         50           800         750         10         60           70         785         750         5           800         770         10         60           80         770         10         60           80         770         10         60           80	ï		Others	$\alpha \cdot (\alpha + Cu_3TI)$ borderline ( $\mathbb{C}$ )	Temperature (C)	Average crystal particle size $(\mu m)$	processing ratio (%)	Heating temperature $(\mathbb{C})$	Holding time (hours)
795         750         5         40           780         750         5         40           770         770         5         40           825         770         10         50           800         770         10         50           795         750         10         50           796         770         10         50           800         770         10         65           810         770         10         66           810         770         5         60           800         750         10         50           800         750         10         50           800         750         10         50           800         750         10         50           9         785         750         50           10         785         750         60           10         780         770         10         60           10         780         770         10         60           10         80         770         10         60           10         80         60	3.2			810	770	10	50	380	9
780         750         5         40           770         750         5         40           825         770         10         50           800         770         10         50           705         750         10         50           706         775         10         60           800         770         10         60           810         750         10         60           810         750         10         60           810         750         10         60           810         750         10         50           805         750         10         60           5         785         750         5         60           60         785         750         10         60           78         785         750         5         30           80         780         750         10         60           80         780         750         10         60           80         780         770         10         60           80         815         770         10         60	2.9			795	750	5	40	400	9
770         750         5         40           825         770         10         50           880         770         10         50           760         750         10         65           800         770         10         65           810         770         10         66           810         770         10         60           810         770         5         40           810         770         5         50           810         770         10         50           805         750         10         60           70         785         750         10         60           805         770         10         60         60           805         770         10         60         60           805         770         10         60         60           805         770         10         60         60           805         770         10         60         60           805         770         10         60         60           80         813         770         10 <td>2.6</td> <td>1</td> <td>1</td> <td>780</td> <td>750</td> <td>5</td> <td>40</td> <td>420</td> <td>9</td>	2.6	1	1	780	750	5	40	420	9
825         770         10         50           800         770         10         50           795         750         10         50           700         750         10         65           800         770         10         65           810         770         10         60           810         770         5         40           810         770         5         40           800         750         10         50           801         750         10         50           802         750         10         60           70         780         750         10         60           80         770         10         60         60           80         770         10         60         60           80         770         10         60         60           80         770         10         60         60           80         770         10         60         60           80         813         770         10         60         60           80         80         770	2.4			770	750	5	40	420	9
800         770         10         50           795         750         10         50           700         750         10         50           775         750         10         65           800         770         10         65           810         770         10         60           810         770         5         40           800         750         10         50           805         750         10         60           70         785         750         10         60           80         780         770         10         60           80         770         10         60         60           80         770         10         60         60           80         770         10         60         60           80         815         770         10         60         60           80         815         770         10         60         60         60           80         810         770         10         60         60         60         60         60         60         60	3.5			825	770	10	50	400	9
795         750         10         50           760         750         10         30           800         770         10         65           810         770         10         60           810         770         5         50           810         770         10         60           810         770         10         50           800         750         750         5         60           70         785         750         10         60         60           80         780         770         10         60         60           80         750         10         60         60         60           80         750         10         60         60         60           80         750         10         60         60         60         60           80         815         770         10         60	3.0	1		800	770	10	50	400	9
760         750         10         30           800         775         750         10         65           800         770         10         65         80           810         750         5         40         80           810         750         10         50         40           810         770         10         50         40           805         750         10         50         80           70         785         750         10         60         80           805         770         10         60         80         80           70         785         770         10         60         80         80           805         770         10         60         60         80	2.9	1	Zn1.0	795	750	10	50	380	10
775         750         10         65           800         770         10         60           810         750         5         50           810         750         10         50           810         770         5         40           805         750         10         50           90         750         10         50           70         785         750         10         60           5         785         750         10         60         10           60         780         770         10         60         10           60         780         10         60         10         60           78         750         10         60         60         10           80         770         10         60         60         10           80         815         770         10         60         60         60           80         815         770         10         60         60         60         60         60         60         60         60         60         60         60         60         60	2.2		Sn0.21	760	750	10	30	380	10
800         770         10         60           810         750         5         50           810         750         10         50           810         770         10         50           800         750         10         50           805         750         10         50           70         785         10         60           70         785         750         60           7         785         770         60           805         770         10         60           70         780         10         60           80         770         10         60           80         770         10         60           80         815         770         10         60           80         815         770         10         60         60           80         815         770         10         60         60         60           80         815         770         10         60         60         60         60         60         60         60         60         60         60         60	2.5	1	Cr0.10	7.7.5	750	10	65	380	9
810         750         50         50           185         750         10         50         40           810         770         5         40         70           805         750         10         50         70           10         805         750         10         50         70           10         785         750         10         60         70           5         785         770         10         60         70           10         780         770         10         60         70           10         780         750         10         60         60           10         780         750         10         60         60           10         780         770         10         60         60         60           20         815         770         10         60         60         60         60           20         815         770         10         60         60         60         60         60         60         60         60         60         60         60         60         60         60         60	3.0		Zr0.15	800	770	10	09	380	9
785         750         10         50         40           810         770         5         40         60           805         750         10         50         60           790         750         5         50         70           60         785         750         10         60         70           5         785         750         10         60         70         70           60         780         770         10         60         70 <t< td=""><td>3.2</td><td>1</td><td>Fe0.20</td><td>810</td><td>750</td><td>5</td><td>50</td><td>400</td><td>9</td></t<>	3.2	1	Fe0.20	810	750	5	50	400	9
810         770         5         40         40           800         750         10         50         80           10         805         750         5         50         80           10         730         750         10         60         80           10         785         750         10         60         80           10         780         770         10         60         80           10         780         750         10         60         80         80           10         780         770         10         60         60         80         80           10         770         10         60         60         80	2.7	1	Ni0.30	785	750	10	20	380	9
800         750         10         50           805         750         5         50           10         730         10         30           10         785         750         60           5         785         750         60           10         785         770         10         60           10         780         750         10         60           10         780         10         60         60           10         815         770         10         60         60           10         770         10         60         60         60           10         770         10         60         60         60           10         770         10         60         60         60           10         770         10         60         60         60         60	3.2		In0.25	810	770	5	40	420	9
805         750         50         50           10         780         750         10         30           5         785         750         10         60           3         735         750         5         30           6         770         10         50         80           10         780         750         10         60         80           5         815         770         10         60         60         80           5         815         770         10         60         60         80         80           5         810         770         10         60         60         8	3.0		Mn0.10	800	750	10	20	380	10
790         750         10         30           60         5         60         60           5         785         750         10         60           3         735         750         5         30           60         780         770         10         60           55         815         770         10         60           65         815         770         10         60           65         815         770         10         60           65         810         770         10         60	3.1	1	P0.07	805	750	5	50	400	10
60         785         750         5         60           54         785         750         10         60           53         735         750         5         30           54         805         770         10         50           55         750         10         60           55         815         770         10         60           56         815         770         10         60           56         810         770         10         60	2.8	•	Si0.13	790	750	10	30	380	9
5,         785         750         10         60           3,         795         750         5         30           6,         805         770         10         50           10         780         750         10         60           5,         815         770         10         60           5,         810         770         10         60	2.7	1	Zn0.70, Cr0.30, Zr0.15	785	750	5	09	380	9
795         750         5         30           805         770         10         50           780         750         10         60           795         750         10         60           815         770         10         60           810         770         10         60	2.7	1	Zn0.50, Fe0.15, P0.05	785	750	10	09	420	9
805         770         10         50           780         750         10         60           795         750         10         60           815         770         10         60           810         770         10         60	2.9		Zn1.2, In0.10, Fe0.16, P0.03	795	750	5	30	420	9
780         750         10         60           795         750         10         60           815         770         10         60           810         770         10         60	3.1	1	Sn0.15, P0.15	805	770	10	50	400	9
795         750         10         60           815         770         10         60           810         770         10         60	2.6	1	Mn0.15, P0.10	780	750	10	99	380	9
815     770     10     60       810     770     10     60	2.9	1	Zn0.80, Ni0.25, Si0.05	795	750	10	09	380	9
810 770 10 60	3.3		Zn1.1, Cr0.15, Zr0.05, Mn0.05	815	770	10	09	380	9
TO A CALL THE PERSON NAMED AND PARTY OF THE PERSON NAMED AND PARTY	3.2	1	Zn0.1, Ni0.25, Sn0.15	810	770	10	09	380	9

# [0059]

# Table 2

	Composit	Composition (unit: % by mass)			Manufac	Manufacturing conditions		
ž			Temperature at	Recrystalli	Recrystallization annealing condition		Aging condition	ion
	Тi	Others	$\alpha$ -( $\alpha$ +Cu <sub>3</sub> Ti) borderline ( $\mathbb{C}$ )	Temperature (C)	Average crystal particle size ( $\mu$ m)	Cold rolling processing ratio (%)	Heating temperature ( $\mathbb C$ )	Holding time (hours)
25	1.0	•	002	089	5	50	400	9
36	1.7	,	735	700	5	. 50	380	9
27	5.5	Ni0.50, Po.15	925	022	10	40	450	9
28	4.5	Zn0.50,Ni1.20, Sn0.50	875	770	10	40	400	9
29	2.8	Zn4.2. Ni1.30. Si0.40	790	750	10	40	380	9
30	3.1	Zn1.5, Ni1.50, Sn1.10, P0.30	805	750	5	50	380	10
31	3.0	•	800	810	25	50	380	9
32	2.9	ı	795	850	30	09	380	9
33	3.2	•	810	750	10	08	360	2
34	2.7	Zn1.0, In0.30, P0.15	785	750	10	06	360	2
35	3.1	Zn1.5, Fe0.35, Mn0.15	805	750	5	09	200	9
36	3.1	Zn1.8, Sn0.50	805	750	10	50	450	20
37	3.0	,	800	770	10	50	650	0.5
38	2.9	1	795	750	10	40	450	0.5
39	2.8	ī	790	750	5	50	200	50

[0060] From these materials obtained by such series of processing, various test pieces were sampled, and the characteristics thereof were tested. First, to evaluate the elastic properties and strength, tensile tests were conducted, and 0.2% proof stress, tensile strength and elongation were measured according to JIS Z 2201 and Z 2241. As for bending properties, test pieces measuring 10 mm wide x 100 mm long were sampled at the transverse angle to the rolling direction, and W-bending tests (JIS H 3110) were conducted at various bending radii, and the minimum bending radius ratio (r/t, r: bending radius, t: test piece thickness (sheet thickness)), not causing cracking, capable of obtaining a favorable bend appearance of rank C or higher in the evaluation standard according to Japan Brass Technical Association standard JBTA T307: 1999 was determined by observing the bend with an optical microscope. This evaluation standard is classified in five ranks; rank A: no wrinkle, rank B: small wrinkle, rank C: large wrinkle, rank D: small crack, and rank E: large crack, and in the case of bending test at larger bending radius ratio than the bending radius ratio for obtaining the result of rank C, appearance of the same or better ranks A to C is obtained. In W-bending test, the bending axis is parallel (Bad Way) to the rolling direction in which the bending properties are inferior. The bending radius is the distance from the center of bending to the inner circumference of the test piece, and the results were evaluated by using a tool having various bending radii.

[0061] Results of characteristic tests are shown in Table 3 (examples) and Table 4 (comparative examples). In examples No. 1 to No. 24, the bending radius ratio (bending radius/sheet thickness) not causing crack as expressed by "a" and 0.2% proof stress expressed by "b", and "a" and "b"

satisfy the relationship " $a \le 0.05xb - 40$ ", and the titanium copper alloy (evaluation: favorable) meeting the recent demands, and well-balanced between high strength and bending properties, could be obtained. In contrast, in comparative examples No. 25 to No. 39, as explained below, the requirements of the invention were not satisfied, and poor bending properties and other problems were found at 0.2% proof stress.

[0062] In No. 25 and 26, since the Ti content is low, high strength of 0.2% proof stress of 800 N/mm² or more is not obtained. In No. 27 and 28, the strength is lower than in the alloy of the example of the invention, and the bending radius ratio is large, and the bending properties are poor. This is because the Ti content is too high, and there is too much precipitation into the grain boundary not contributing to enhancement of strength, and it seems cracks are initiated from the precipitates in the grain boundary at the time of performing tension tests and bending tests.

[0063] No. 29 has too high amount of Zn, and No. 30 has too high a total amount of subsidiary additives, and they are both low in electrical conductivity and poor in bending properties. No. 31 and 32 are examples of extremely high recrystallization temperature, in which average grain size of  $20 \,\mu m$  or less was not obtained, and high 0.2% proof stress could not be obtained. When compared with an alloy example of 0.2% proof stress of the same level in the invention, the bending radius ratio is large and bending properties are poor. No. 31 is a mixed grain matrix.

Accordingly, the average grain size in No. 31 is  $25 \mu m$ , being smaller than in No. 32, but the bending radius ratio varied in a range of 3.0 to 5.0. The maximum value is recorded in Table 4.

[0064] No. 33 and 34 are examples of too high working ratio of cold rolling, but by shortening the aging period, a high 0.2% proof stress was

obtained, however, the bending properties were poor. No. 35 is an example of low aging temperature, and since the temperature is low, the aging effect is insufficient, and the strength is low. No. 36 is an example of too long aging period, and 0.2% proof stress is lowered due to overaging.

[0065] No. 37 is an example of too high aging temperature and too short aging period, and since the aging temperature is too high, the solid solution amount of Ti is excessive, and since the aging period is short, sufficient 0.2% proof stress is not obtained. No. 38 is an example of short aging period, and the aging effect is insufficient, and the 0.2% proof stress is low. No. 39 is an example of low aging temperature, and in spite of long aging period of 50 hours, high 0.2% proof stress is not obtained.

[0066] Therefore, in the alloy examples of the invention, by recrystallization annealing (solution treatment) at a temperature below the  $\alpha$ -( $\alpha$ +Cu<sub>3</sub>Ti) borderline in an appropriate composition, and performing the subsequent cold rolling and aging process in adequate conditions, a favorable relation of 0.2% proof stress and bending radius ratio is obtained, and titanium copper alloy of high strength is obtained without sacrificing the bending properties. In contrast, in alloys of comparative examples, as compared with alloys of the invention, favorable relation of 0.2% proof stress and bending radius ratio is not obtained, and material with good balance is not produced.

[0067]

Table 3

	Tensile	0.2% proof			Bending radius	Electrical
No.	strength	stress (b)	Elongation (%)	0.05 x b-40	ratio (r / t)	Conductivity
1	Q1/2\	(N/mm <sup>2</sup> )	(,			(%IACS)
	(N/mm²)	900	15	5.0	3.0	14.4
	1050		17	4.0	2.0	14.3
2	1030	880	15	5.0	2.0	14.1
3	1030	900	16	5.0	2.0	14.3
4	1020	900	15	7.0	3.0	13.6
5	1050	940	14	8.0	3.0	13.2
6	1070	960	17	4.5	3.0	14.2
7	1030	890	23	1.5	1.0	15.3
8	880	830	18	4.0	3.0	13.4
9	970	880	17	5.0	3.0	14.4
10	1010	900	17	6.0	3.0	14.5
11	1060	920		5.5	3.0	14.5
12	1030	910	15		4.0	13.4
13	1070	930	10	6.5	3.0	13.4
14	1040	910	15	5.5	3.0	13.7
15	1040	920	14	6.0		13.5
16	950	850	20	2.5	0.0	14.7
17	1110	950	8	7.5	4.0	14.0
18	1010	900	14	5.0	3.0	15.1
19	970	860	18	3.0	1.0	14.0
20	1060	940	10	7.0	3.0	14.4
21	990	900	12	5.0	4.0	
22	1050	930	11	6.5	3.0	13.7
23	1080	990	8	9.5	4.0	14.7
24	1040	930	11	6.5	4.0	14.6

[0068]

Table 4

				100		
1	Tensile	0.2% proof			Bending radius	Electrical
No.			Elongation	0.05 x b-40	ratio	Conductivity
140.	strength	stress (b)	(04)		(r / t)	
	277 %	(N/mm²)	(%)			(%IACS)
	(N/mm <sup>2</sup> )		11		5.0	35.0
25	680	600	8	· .	5.0	20.3
26	790	710	1 0	<del>                                     </del>	8.0	10.4
27	750	720	2		7.0	10.3
28	800	750	8	3.0	5.0	8.3
29	960	860		2.0	5.0	7.1
30	950	840	10		5.0	14.3
31	850	760	25		4.0	14.4
32	880	800	20	0.0	>10.0	15.3
33	1150	970	10	8.5	>10.0	15.1
34	1180	990	15	9.5	3.0	12.1
35	820	750	3	ļ <u>.</u>		15.2
36	890	780	20	-	3.0	15.1
37	800	720	18	<u> </u>	1.0	12.3
38	850	760	7	<u> </u>	4.0	12.4
39	820	750	7		3.0	12.4

### (Example 2)

[0069] Test pieces were press worked at the process conducted up to cold rolling in the same condition as in examples No. 2 and No. 10 in example 1 except that the final recrystallization annealing was conducted in the conditions as shown in Table 5. The press worked test pieces were evaluated by W-bending test in the same condition as in example 1, and then were subjected to aging. The aging conditions were  $400^{\circ}$ C and 6 hours in No. 2, and  $380^{\circ}$ C and 6 hours in No. 10. Before and after the aging process, characteristics of test pieces were examined using the same method as in example 1, and the results are shown in Table 5. As is clear from Table 5, when the average grain size is in a range of 5 to 15  $\mu$ m, the bending radius ratio (r/t) is zero, and an extremely superior bending properties were confirmed. In these test pieces, the hardness after aging process was 310 Hv or more, and the tensile strength was 1000 MPa or more.

[0070] Table 5

:	Evaluation	Bending inferior	Superior	Superior	Superior	Superior	Bending	inferior	Bending	IIIICIIOI	Superior	Cusarior	Superior	Superior		Superior	Bending	Interior
	Hardness Hv	300	315	320	310	315	310	010	300		310	;	315	310		310	300	
ging process	Electrical Conductivity %IACS	13.7	14.3	12.5	13.7	14.1		6.8	13.7		14.2		13.9	14.4		14.0	8.0	2
Characteristics after aging process	Elongation %	10	1.7	12	13	13	2	14	ç	OI	15		15	17		15	;	17
Charac	0.2% proof stress	900	000	000	040	000	940	854	į	870	920		940	98	ann	006		880
	Tensile strength MPa	070	200	1030	CONT.	1030	1020	972		086	1015	TOTAL	1020	9.6.	1010	1015		066
S	MBR/t	c	7	0	9	0	0	73		63	•		0		0	-		22
Characteristic before aging process	Electrical Conductivity	winds.	٠	4	4	4	4	າວ		81		3	8		က	,	ç	4
aracteristic bef	Elongation	%	_	2	2	2	1	-	,	_		<b>63</b>	6	,	2		-	1
E		MPa	820	790	785	770	760	670	0,0	820		780	066	2)	780	1	760	069
	Average crystal particle	11 71	က	22	0	2	15	8	77	673	,	2	,	χ	10		15	20
lization		sec.	30	45	9	8	120		180	06	3	40		09	98		120	150
Recrystallization	annealing condition Holding C time		750	750	35	750	750	3	750	02.6	-	770	1.	0//	770		770	07.7
	Composition wt%		2.9Ti-Cu	J. San	17-116-7	2.911-Cu	2.911-02	7.911-Cu	2.9Ti-Cu	3.0Ti-0.15Zr-	Cu	3.0Ti-0.15Zr-	Cu	5.011-0.1021. Cu	3.0Ti-0.15Zr-	Çn	3.0Ti-0.15Zr- Cu	3.0Ti-0.15Zr-
	No.		-	,	7	<sub>ا</sub> ا	4,	c	9		7	α	$\top$	6	1	er	п	12

#### (Example 3)

[0071] Electrolytic cathode copper or oxygen-free copper, and metal lump of additive elements or master alloy were used as raw materials, and copper alloy ingots of various compositions shown in Table 6 (examples) and Table 7 (comparative examples) were melted in a high frequency melting furnace. Hot tops of these ingots (measuring 50 mm thick x 100 mm wide x 150 mm long, weighing about 7000 g) were cut off, and after removing the surface layer, they were heated for 1 hour or more at 850°C, and the material was hot rolled to a thickness of 8 mm while keeping the temperature at 600°C or more, and it was cooled in water. The material temperature in hot rolling was measured by two-color pyrometer preliminarily compensated for temperature. The surface oxide scale was removed by machine polishing in a thickness of about 0.4 mm on one side, and the plate was cold rolled to a specified thickness of less than 0.4 mm (working ratio 95% or more), and the material surface was degreased by an organic solvent such as acetone, and specified aging was processed in a vacuum annealing furnace, and the sample materials were thereby prepared.

[0072]

Table 6Composition and manufacturing conditions of high strength titanium copper alloys of the invention

	Com	position (wt%)		Man	ufacturing cond	itions	
No.			Hot rolling	condition	Cold	Aging	process
	Ti	Others	Min.material temperature (°C)	Final thickness (mm)	rolling processing ratio (%)	Temperature (°C)	Holding time (hr)
1	2.3	-	680	8.0	97	380	6
2	2,6	-	700	8.0	98	380	6
3	2,9		730	8.5	97	380	10
4	3.2	-	700	8.0	97	380	10
5	3.4	_	710	7.5	97	360	6
6	3.5	-	730	8.0	97	360	6
7	2.9	Zn1.0, Fe0.20	700	8.0	97	400	6
8	2.6	Sn0.21	700	8.5	98	380	6
9	2.5	Cr0.10	710	7.5	96	420	6
10	3,0	Zr0.15	700	7.5	97	380	10
11	3.2	Fe0.20	720	8.0	97	360	8
12	2,7	Ni0.30	700	8.0	97	380	6
13	3.2	In0,25	680	8.0	97	380	6
14	3.0	Mn0.10	700	8.5	96	380	6
15	3.1	P0.07	700	8.5	98	360	8
16	2.8	Si0.13	710	8.0	97	420	6
17	2.7	Zn0.7, Cr0.30, Zr0.15	710	8.0	97	400	6
18	2.9	Zn1.2, In0.10, Fe0.16, P0.03	730	8.0	97	380	6
19	3.1	Sn0.15, P0.15	720	7.5	96	420	6
20	2.6	Mn0.15, P0.10	700	7.5	99	360	4
21	2.9	Zn0.8, Ni0.25, Si0.05	740	8.0	97	360	8
22	3.3	Zn1.1, Cr0.15, Zr0.05, Mn0.05	750	8.0	97	380	10
23	3,2	Zn0.1, Ni0.25, Sn0.15	710	8.0	97	380	6

[0073]

Table 7
Composition and manufacturing conditions of alloys of comparative examples

	Com	position (wt%)		Man	ufacturing cond	itions	
			Hot rolling	condition	Cold	Aging	process
No.	Ti	Others	Min. material temperature (°C)	Final thickness (mm)	rolling processing ratio (%)	Temperature (°C)	Holding time (hr)
24	1.5	-	680	8.0	97	420	6
25	0.009	Zn1.5, Cr0.30, Zr0.15	680	8.0	97	420	6
26	5.5	Ni0.50, P0.15	720	35	*)(	Cracked during he	ot rolling
27	4.0	Zn0.5, Ni1.20, Si0.50	720	8.5	*) C	Cracked during co	ld rolling
28	2.8	Zn4.2, Ni1.30, Si0.40	700	8.0	96	380	6
29	3.1	Zn1.5, Ni1.50, Sn1.10, P0.30	700	8.0	96	380	6
30	3.0		580	25	*)(	Cracked during he	ot rolling
31	2.9	Zn1.5	580	15	*) (	racked during co	
32	3.2	-	700	10	85	360	6
33	2.7	Zn1.0, In0.30, P0.15	720	10	90	360	6
34	3.1	Zn1.5, Fe0.35, Mn0.15	700	8.0	97	200	6
35	3.1	Zn1.8, Sn0.50	700	8.0	96	450	50
36	3.0	-	700	8.5	98	650	0.5
37	2.9	-	720	8.5	98	450	0.5
38	2.8	-	750	8.0	96	200	50
39	2.9	-	730	8.5	97	-	-
40	3.2	_	700	8.0	97	-	-

<sup>\*)</sup> Not examined after cracking

[0074] From the sheet obtained in this manufacturing process, various test pieces were sampled, and were subjected to material tests. The strength was evaluated by the tensile test according to JIS Z 2241, and the 0.2% proof stress, tensile strength, and elongation were evaluated. The test pieces were No. 13B type test pieces conforming to JIS Z 2201. The electrical conductivity was measured according to JIS H 0505. Results of measurements are shown in Tables 8 and 9.

Table 8 Evaluation of high strength titanium copper alloys of the invention

No.	Tensile strength (MPa)	0.2% proof stress (MPa)	Elongation (%)	Electrical Conductivity (%I ACS)	Evaluation
1	1230	1180	3	10.2	Superior
2	1270	1220	3	11.3	Superior
3	1290	1240	2	11.2	Superior
4	1310	1260	2	10.3	Superior
5	1300	1220	2	11.4	Superior
6	1310	1240	2	10.3	Superior
7	1290	1220	3	11.5	Superior
8	1300	1250	3	10.4	Superior
9	1260	1200	4	10.3	Superior
10	1280	1220	3	11.7	Superior
11	1270	1200	2	11.2	Superior
12	1250	1180	4	12.3	Superior
13	1290	1210	3	12.2	Superior
14	1280	1230	3	11.1	Superior
15	1310	1250	2	10.0	Superior
16	1270	1210	3	11.1	Superior
17	1280	1210	3	12.0	Superior
18	1290	1230	2	10.8	Superior
19	1260	1200	4	11.6	Superior
20	1300	1240	3	10.4	Superior
21	1280	1220	3	12.1	Superior
22	1280	1230	2	12.0	Superior
23	1270	1220	2	11.7	Superior

[0076]

Table 9

Evaluation of high strength titanium copper alloys of comparative examples

No.	Tensile strength (MPa)	0.2% proof stress (MPa)	Elongation (%)	Electrical Conductivity (%I ACS)	Evaluation
24	780	720	2	26.4	Poor
25	800	720	2	55.1	Poor
26	-	-	-	-	Not evaluated
27	_	-	-	-	Not evaluated
28	1280	1220	1	8.0	Poor
29	1280	1220	1	7.8	Poor
30	-	-	-	-	Not evaluated
31	-	_	-	-	Not evaluated
32	1160	1090	1	10.3	Poor
33	1180	1100	1	10.1	Poor
34	1210	1100	1	5.7	Poor
35	1040	940	2	13.2	Poor
36	1060	1000	1	13.1	Poor
37	1250	1160	1	8.0	Poor
38	1230	1130	1	5.8	Poor
39	1220	1120	1	6.0	Poor
40	1250	1160	2	5.8	Poor

[0077] All examples of the invention in Table 8 recorded a tensile strength of 1200 MPa or more as required in a fork-shaped connector, and in particular, examples Nos. 4 to 6, 8, 15, and 20 exhibited a tensile strength of 1300 MPa or more. However, in the comparative examples shown in Table 9, No. 26, 27, 30, and 31 cracked during hot or cold rolling, and the manufacturing efficiency was poor, and the characteristics thereof could not be evaluated. That is, No. 26 and 27 were too high in Ti content, and No. 26 cracked in hot rolling, and although hot rolled to a thickness of 35 mm, subsequent processing was not continued. No. 27 did not crack in hot rolling; however, edge cracking occurred in the subsequent cold rolling. No. 30 and 31 were low in aging temperature, and the temperature was below 600°C at a thickness of 25 mm and 15 mm, respectively, and edge cracking occurred in cold rolling after hot rolling.

[0078] No. 24 is low in Ti content, and it is hence low in strength. No. 25 is also low in Ti content, and it is an example of a Cu-Cr-Zr copper alloy, and although the electrical conductivity is high, the strength is low. No.

28 and 29 are high in contents of Zn and others, and the electrical conductivity is low, and No. 29 formed edge cracking during cold rolling. [0079] No. 32 and 33 are too low in workability of cold rolling, and the strength is low. No. 34 and 38 are low in aging temperature, and in spite of a long aging period of 50 hours for No. 38, desired electrical conductivity is not achieved. No. 37 has a short aging period, and desired electrical conductivity is not achieved. Nos. 35 and 36 are high in aging temperature or have long aging periods, and also because the working ratio of cold rolling before the aging process is high, it results in over-aging, and high strength is not obtained.

[0080] Nos. 39 and 40 are similar to alloys of Nos. 3 and 4 of the invention manufactured in the same process up to cold rolling, but are not aged, and although a high strength of 1200 MPa or more is obtained by cold rolling at high working ratio, the electrical conductivity is low, and they cannot be used in fork-shaped connector.

[0081] Thus, the titanium copper of the invention can be obtained only by the manufacturing method of the invention, and it is a titanium copper alloy having a tensile strength of 1200 MPa or more and an electrical conductivity of 10% IACS or more, not obtainable in the conventional art. The fork-shaped connector using the high strength titanium copper of the invention has a contact pressure equivalent to that of beryllium copper. (Example 4)

[0082] Of the materials manufactured up to the cold rolling processing in Table 6 in example 3, those listed in Table 10 were selected and press worked. These press worked test pieces were aged in the same condition as in example 3. Characteristics of test pieces were investigated before and after the aging process in the same method as in example 3, and the

results are recorded in Table 10. To evaluate the thermal expansion and shrinkage rate, a test piece of 100 mm x 10 mm was cut out in a parallel direction to rolling direction, the distance between specified marking positions was measured by using a three-dimensional coordinate measuring apparatus, and the marking position distance was measured again after the aging process, and the dimension change rate was determined from the measurements before and after heating. By way of comparison, using the material shown in Table 7 and beryllium copper, test pieces were prepared under the same condition aforementioned, and the characteristics were measured in the same method. The results are shown in Table 10. [0083]

Evaluation of high strength titanium copper alloys of the invention

Table 10

			Т	Т	7		Т	7	_		_	Т		1	$\neg$	$\neg \top$		Т		رو	
,	Evaluation	Superior	Superior	Superior	Superior	Superior	Superior	Superior	Superior	Superior		Superior	Superior	Poor	Poor	Poor	Poor		Poor	Shrinkage	inferior
Thermal expansion/	shrinkage %	90.0	0.05	50.0	0.0	90:0	90.0	90.0	0.05	0.05	200	0.06	0.05	0.04	0.05	0.04	0.05		0.05		0.11
	Hardness Hv	350	098	230	3/0	360	350	350	360	37		350	350	250	340	320	320		310	18	380
ng process	Electrical Conductivity %I ACS	10	=	11	11	12	10	11	12	10		12	12	56	8	10	9		13	;	25
Characteristic after aging process	Elongation %	۲	, ,	7	2	3	4	2	3	,	7	4	3	2	1	-		•	2		3
Charact	0.2% proof stress MPa	1100	0011	1240	1220	1220	1200	1200	1210	1250	1770	1200	1220	720	1220	1100	91	3	046		1200
	Tensile strength MPa	0000	UC71	1290	1300	1290	1260	1270	1300	0671	1310	1260	1280	780	1280	1180	0.01	0171	1040		1300
ging process	Electrical Conductivity	/01 //O	,	7	5	2	4	0		0	4	s	4	7	3	\$	,	n	,	,	91
Characteristic before aging process	Elongation %		2	2	1	_	,	7 -	-   .	- ;	2		2	6	_	-		<b>~</b> 1	,	•	15
Characte	Tensile strength	Mra	1100	1170	1180	1160	9	0+11	OCT	1160	1180	1140	1160	650	1140	1090		1170		No.	260
	Composition wt%		2.3Ti	2.9Ti	3.4Ti	2.9Ti-1.0Zn-	0.2re	2.511-0.10Cr	3.211-0.20re	3.2Ti-0.25In	3.1Ti-0.07P	3.1Ti-0.15Sn- 0.10P	2.9Ti-0.8Zn-	1 5Ti	2.8Ti-4.2Zn- 1.30Ni-0.40Sn	2.7Ti-1.0Zn- 0.30In-0.15P	3.1Ti-1.5Zn-	0.35Fe-	3.1Ti-1.8Zn-	0.50Sn	1.9Be-0.25Co-
	No.		-	2	3	4	1	十	1		8	6	91	F		13		4	,	cı	ì

[0084] As can be seen from Table 10, in Nos. 1 to 10 in example 4, the strength after the aging process was equivalent to that of beryllium copper (No. 16), and a high electrical conductivity was obtained. In contrast, with No. 11, the titanium content was less than 2.0% by mass, and the tensile strength was low. In No. 16, the thermal expansion and shrinkage rates were extremely large.

[0085] According to the invention, as described herein, the titanium copper alloy is increased in strength without sacrificing the bending properties, and the required characteristics as the terminal connector for electronic component can be improved, so that a material for a terminal connector of high reliability can be presented. In the examples of the invention, the titanium copper alloy has a tensile strength of 1200 MPa or more and an electrical conductivity of 10% IACS, and it is increased in strength to a level equal to that of beryllium copper, and it is improved so as to be a copper alloy suited for use in terminal connectors for electronic component, in particular, for fork-shaped connector for FPCs, and it is shown to be usable sufficiently as a substitute copper alloy for beryllium copper alloy. IN addition, if the contact of the terminal connector is plated before or after working, the strength is hardly changed, and the effects of the invention are unchanged.